

PCTWORLD INTELLECTUAL PROPERTY
International

INTERNATIONAL APPLICATION PUBLISHED UNDER

WO 9606953A1

(51) International Patent Classification ⁶ : C14C 1/04, 1/08		A1	(11) International Publication Number: WO 96/06953
			(43) International Publication Date: 7 March 1996 (07.03.96)
(21) International Application Number: PCT/AU95/00566 (22) International Filing Date: 1 September 1995 (01.09.95) (30) Priority Data: PM 7804 1 September 1994 (01.09.94) AU (71) Applicants (for all designated States except US): COMMON-WEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; 407 Royal Parade, Parkville, VIC 3052 (AU). THE FEDERATED TANNERS ASSOCIATION OF AUSTRALIA [AU/AU]; 9th floor, National Mutual Centre, 15 London Circuit, Canberra, ACT 2601 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): POJER, Peter, Michael [AU/AU]; 27 Fitzgibbon Crescent, North Caulfield, VIC 3161 (AU). HUYNH, Chi, Phuong [AU/AU]; 325 Gladstone Road, Dandenong North, VIC 3175 (AU). (74) Agent: McCORMACK, John, David; Griffith Hack & Co, 509 St Kilda Road, Melbourne, VIC 3004 (AU).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published With international search report.	
(54) Title: PICKLING OF HIDES AND SKINS			
(57) Abstract A pretreatment method in the tanning process for modifying the properties of a hide of skin of an animal is disclosed in which the pretreatment step comprises contacting the hide or skin with a pickling solution formed from a pickling agent which comprises at least one or more of phenol mono-, di- or trisulphonic acid or derivatives thereof, either singly or in combination, including combinations with other materials, which treatment is effective at a final pH of or below 3.4, and there is even penetration of the pickling solution into the hide or skin without swelling taking place in the absence of added salt. The advantage of the pickling solution and method of treatment as described is that a low salt content effluent is produced.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

PICKLING OF HIDES AND SKINS

The present invention relates generally to natural products, particularly natural products requiring treatment before they may be used in a functional manner. More particularly, the present invention relates to natural products obtained from animals, such as for example skins, hides and the like. Even more particularly, the present invention relates to a process for pickling hides and skins as part of the tanning process, and to a method for preparing a pickling solution. The present invention finds particular application in pickling and tanning naturally occurring hides or skins to produce durable leather.

Although the present invention will be described with particular reference to a pickling solution for use in treating hides and skins of animals, it is to be noted that the scope of the present invention is not so limited, but rather the scope is more extensive so as to include other pickling solutions and uses of the pickling solution other than those specifically described.

Leather is a natural product which is derived from the hides or skins of many animals. However, before the hides or skins are useful, they must be treated. One such treatment is tanning. Hides and skins need to be tanned in order to produce leather which has the durability and thermal stability normally required of leather goods, which is to say that the properties of the hides and skins need to be modified before they are useful, which modification is achieved by tanning. The most widely practised tanning procedure involves treatment of the hides and skins with chromium salts. However, to promote uniform penetration of

- 2 -

the chromium salts into the collagen matrix of the skins and hides without precipitation, the hides and skins require a pickling or acidification treatment or pretreatment. Traditionally, the pickling or acidification treatment involves the use of a mineral acid, such as for example hydrochloric acid, sulphuric acid or the like, or an organic acid, such as formic acid, or more commonly a mixture of sulphuric and formic acids, together with the addition of a salt, usually sodium chloride, to prevent swelling of the hides or skins which would otherwise occur when the collagen is exposed to an acid medium. Although traditional pickling treatments are effective and employ materials which are inexpensive, such treatments suffer from serious disadvantages in that they result in the production of tannery effluents which have a high salt concentration. The disposal of the high salt effluent presents a serious environmental problem, particularly for tanneries situated in-land, or in areas where there is insufficient water or rainfall to effectively dilute the effluent to acceptable levels for safe or convenient disposal.

In the past, attempts to overcome this disadvantage have involved the use of various organic sulphonc acids as replacements for the salts to suppress the swelling which accompanies pickling the hides or skins with agents such as sulphuric and/or formic acid. In one particular instance, a condensate of a sulphonated phenol with a formaldehyde-urea prepolymer had been considered as a salt alternative. Other attempts have led to the introduction of commercially available pickling agents such as PICALTAL marketed by BASF, SELLATAN P from Ciba-Geigy, and other similar materials which are examples which are based on naphthalene sulphonc acids or oligomeric phenol sulphonc acid sulphones which are useful in reducing or counteracting the tendency towards swelling whilst allowing tanning of the hides or skins to take place. Unfortunately, the use of

- 3 -

such materials has a major disadvantage in that they tend to become ineffective in acidic conditions of below about pH 3, or otherwise impart undesirable characteristics, such as fullness or stiffness, to the pickled stock, or hinder the rate of or uniformity of penetration of the collagen matrix, all of which result in uneven pickling of the hides or skins or in the skins or hides exhibiting some other undesirable property.

In the past, among the compounds investigated by other workers in attempts to replace salt in pickling solutions were phenol sulphonic acids. However, the results of these previous investigations obtained at that time were not encouraging and tended to indicate that the sulphonic acids tested might not be suitable as alternatives to salt in pickling treatments prior to tanning. In fact, some investigators found that phenol sulphonic acid gave swelling values that were close to those obtained when using sulphuric acid in the absence of any additional salt, which clearly indicated the unsuitability of these materials. This was confirmed by other investigators who found that marked swelling occurred when hides were pickled with phenol sulphonic acid. It is to be noted that hides pickled with sulphuric acid alone will swell in excess of 50% of the delimed weight of the hide whereas when a salt/sulphuric acid mixture is used not only is there no swelling but there is also deswelling to about -10% of the original delimed weight of the hide.

Therefore, there was a need for a pickling solution which was as least as effective as the traditional sulphuric acid/salt treatment but which did not result in an effluent of high salt concentration. Furthermore, there was a need for an alternative pickling agent to traditional agents which produced desirable characteristics in the leather.

Surprisingly, it has now been found that phenol mono-, di-

- 4 -

and trisulphonic acids either alone or in combination with each other in the absence of excess or large amounts of sulphuric acid, give deswelling of hides and skins comparable to that obtained when using conventional pickling regimes involving the use of salt or involving the use of commercially available salt-alternative treatments as mentioned previously. More importantly, it has been discovered that such sulphonic acids do not possess the undesirable properties of the prior art compounds, which made using such prior art compounds inconvenient to the tanner. Furthermore, it has been discovered that the leather products exhibited no undesirable properties. In addition, it was discovered that the phenol mono-, di- and trisulphonic acids of the present invention could be added rapidly to the skins or hides being treated without swelling taking place since such materials rapidly penetrated the collagen matrix and were effective at a pH below 3 without causing swelling of the skin or hides.

Therefore, it is an aim of the present invention to provide a pickling agent which is useful for pickling hides or skins, which results in leather products having desirable properties, but which does not produce an effluent having an unacceptably high salt content. Additionally, it is an aim of the present invention to provide a method of making a pickling agent having desirable properties.

According to a first aspect of the present invention there is provided a method of treating a naturally derived product prior to performing a subsequent treatment wherein the naturally derived product is treated with an agent to modify a property or characteristic of the naturally derived product, characterised in that the treatment by the agent is effective at a final pH of or below 3.4 and in that the agent comprises at least one or more of phenol mono-, di- or trisulphonic acid or derivatives thereof, either singly or in combination, including combination with

- 5 -

other materials.

According to a further aspect of the present invention there is provided a method of preparing a treatment agent suitable for use in treating a naturally derived product comprising contacting a phenol mono-, di- or trisulphonic acid or derivative thereof, either singly or in combination, including combination with other materials including oleum or a sulphuric acid, characterised in that the agent is effective in use at a final pH of 3.4 or less.

Typically, the naturally derived product is a hide or skin, more typically a hide or skin useful in producing leather or a leather product.

Typically, the treatment agent for use with the hide or skin is a pickling or acidifying agent. Typically, the subsequent treatment is a tanning treatment. Typically, the tanning treatment can be any type of tanning treatment or more particularly a chromium tanning treatment or vegetable tanning treatment.

Typically, the agent is a pickling agent and comprises essentially pure phenol mono-, di- or trisulphonic acid or derivatives thereof. More typically, the pickling agent comprises a further acidic material. Typically, the further acidic material is sulphuric acid or oleum or a material derived from them.

By use of the term "essentially pure" in the context of the present invention is meant a phenol sulphonic acid agent which before application to the hides or skins is associated with up to and no more than about 1 g, preferably less than about 0.6 g, more preferably less than about 0.4 g of sulphuric acid, oleum or equivalent thereof per 1 g of the phenol sulphonic acid or mixture thereof.

- 6 -

By use of the term "derivatives" is meant any salt or partial salt or compound of the phenol sulphonic acids, or any such derivatives having functional groups equivalent to the phenol sulphonic acids, such as for example compounds
5 having a benzene ring substituted with a sulphonic acid, carboxylate, ester, alkyl, hydroxyl or thiol group.

More typically, the pickling agent comprises a mixture of monosulphonic acid and disulphonic acid, optionally together with trisulphonic acid, or any combination
10 thereof.

Typically, the amount of disulphonic acid in the agent is maximised in order to facilitate reduction in the amount of swelling. More typically, the ratio of monosulphonic acid to disulphonic acid is from about 100:1 to 1:100,
15 preferably about 50:1 to 1:50, more preferably about 1:1 by weight. However, the relative ratios of disulphonic to monosulphonic acid can deviate from these ranges. It is to be noted that phenol trisulphonic acid can be present as well as phenol monosulphonic acid and disulphonic acid.

20 Typically, phenol sulphonic acids or mixtures of the present invention contain less than 1 g sulphuric acid or oleum per gram of phenol sulphonic acid, and are readily prepared when phenols are sulphonated with oleum and/or sulphuric acid.

25 Typically, the pickling treatment can have a duration of up to about 48 hours or more, typically up to about 24 hours.

In one embodiment of the present invention, when oleum is used as a sulphonating agent, the concentration of the sulphonic acid in the resultant product mix is increased.
30 It is to be noted that the amount of phenol di- and trisulphonic acid relative to the amount of monosulphonic acid is increased. However, the amount of phenol

- 7 -

trisulphonic acid is relatively small compared to the amounts of phenol mono- and disulphonic acids. The concentration of sulphur trioxide in the oleum can, of course, be varied, and while the use of oleum containing, say, 65% sulphur trioxide will give a very effective pickling agent, it has to be kept in mind that because the product will contain less associated sulphuric acid, more of the pickling agent will have to be used in the pickling treatment to achieve the desired level of acidification. In practice, for most purposes, oleum typically containing about 20% to 25% sulphur trioxide is effective.

In another embodiment, reaction temperatures for producing the pickling agent of the present invention will typically be in the range of from 0°C to 200°C, preferably in the range 80°C to 140°C. In addition, it is preferred to use in excess of 2 moles of sulphuric acid in the reaction mixture to maximise the amount of phenol disulphonic acid, and optionally to assist in acidification of the pickling step.

Typically, the final pH of the pickled hides or skins is about 3.0 or below.

Typically, the method of treatment and the pickling agent of the present invention may be applied to any of the types or hides or skins currently being processed by conventional techniques, such as for example ovine, porcine, bovine, caprine or like hides or skins, whether green or preserved in any known manner. More typically, the hide or skin may be treated by the pickling agent of the present invention either before or after the hair, wool or other covering or associated material has been removed. Even more typically, the process of the present invention can be used in conjunction or in combination with other technologies or processes conventionally used to prepare hides and skins for tanning.

- 8 -

Typically, the amount of phenol sulphonic acid or acids or mixtures thereof or derivatives thereof to be used may vary widely, but as in conventional acid/salt treatments, the amount used will depend to some extent on the state of the hide or skin to be pickled, the amount of mineral acid or separately introduced organic acid in the preparation, and the desired end pH or the like. Typically, for full thickness delimed hides, 1% to 10% by weight, based on the weight of the delimed hide, of the sulphonic acid or mixture will give satisfactory pickling.

Typically, the hide or skin may be in contact with the phenol sulphonic acid or acids or mixtures thereof for any suitable period, depending on requirements and/or be at any suitable or convenient temperature. For example, delimed hides treated with a pickling solution containing from about 1% to 10% by weight acid will lead to equilibrium pickles exhibiting no swelling in less than 24 hours. Additionally, uniform and even chromium penetration and no swelling of the hides or skins will be exhibited when the chromium or chromium-containing tanning material is applied simultaneously or substantially simultaneously or sequentially with the sulphonic acid or acids or mixtures thereof.

The invention will now be described by way of example with reference to the following examples, which are understood to be illustrative only of the scope of the present invention and not to be taken as restrictive on the generality of the invention described therein.

Further, it is to be noted that in Examples 4 to 8, the reagent weight percentages are based on the weight of the damp delimed hides or skins being treated.

- 9 -

EXAMPLE 1Preparation of phenol sulphonic acid solution using 22% oleum

To prepare this example of the pickling agent 683 ml of 22%
5 oleum solution was slowly added to 650 g of phenol in a
suitable vessel with cooling and stirring while maintaining
the reaction temperature below 80°C. After all of the
oleum had been added, the mixture was warmed to 80°C and
maintained at that temperature whilst stirred for 12 hours.
10 The mixture was then cooled and water was added to make a
final volume of 2 L. The resultant solution contained
approximately 60% of a phenol sulphonic acid mixture
comprising about 1:1 weight ratio of mono- to disulphonic
acids.

15 EXAMPLE 2Preparation of phenol sulphonic acid solution using sulphuric acid

Concentrated sulphuric acid (2.34 kg) was added slowly with
stirring to phenol (1 kg). The temperature rose to 80°C.
20 The mixture was maintained at 120°C for a further 2 to 12
hours. It was cooled and water was added to make up a
final volume of 3.08 L.

Analysis showed that this mixture comprised of
approximately equimolar quantities of phenol mono- and
25 phenol disulphonic acids.

EXAMPLE 3Preparation of concentrated phenol sulphonic acid solution

A phenol sulphonic acid mixture was prepared as in Example
1 but this time using 65% oleum instead of 22% oleum. The
30 result was a greater concentration of the phenol sulphonic
acids and less sulphuric acid being present in the reaction
mixture. Also more phenol disulphonic acid was produced
than the amount of phenol monosulphonic acid and also a

- 10 -

small amount of trisulphonic acid was produced. For use in the pickling agent, the mixture was diluted to give about a 60% solution of sulphonic acids as in Example 1.

EXAMPLE 4

Equilibrium pickling of full thickness hide

In this example a pickling agent prepared in accordance with the preceding examples was employed to pickle a full thickness hides. A solution of water (35% by weight based on the weight of the delimed hides as indicated previously) and sodium formate (0.5% by weight based on the weight of the delimed hides as indicated previously) was added to delimed hides, which were then drummed for 5 minutes in a suitable drum before adding the solution containing the pickling agent of phenol sulphonic acid mixture as prepared in accordance with Example 1 or Example 2 at a concentration of 4% of the formulation based on the weight of the delimed hides in 10% water by weight based on the weight of the delimed hides as indicated previously. Drumming was continued for 2 to 3 hours, after which formic acid (0.85% by weight based on the weight of the delimed hides as indicated previously) and a suitable amount of sulphuric acid depending on the final pH desired was added. Drumming was continued for a further 12 hours. The pH of the pickling liquor was from about 1.5 to 3, depending on the extent of deliming of the hides and the amount of sulphuric acid added previously. A sample cut was taken from the hide which showed that full penetration of the pickling agent had been achieved. No swelling of the hide was observed.

EXAMPLE 5

Non-equilibrium pickle of hides combined with chromium tannage

A solution of water and sodium formate was prepared and added to delimed hides as in Example 4, followed by the addition of the phenol sulphonic acid solution to the hides

- 11 -

also in accordance with Example 4. After drumming for 30 minutes, formic acid (0.85%) was added and sulphuric acid as in Example 4 and drumming continued for a further 30 minutes. 8% by weight of a "33% basic" chromium tanning material (i.e. a tanning powder comprising chromium sulphate in which one third of the sulphate ion content had been replaced by hydroxyl ion) was then added to the drumming vessel and the mixture further drummed. Full penetration was noted after 5 to 7 hours by observing a sample removed from the hide. The pH of the tanning solution was raised to 3.5 to 4.2 by adding magnesium oxide (0.5% to 1.5% depending on the final pH desired). The hides were drained and washed. Shrinkage temperature of the tanned material was $>100^{\circ}\text{C}$.

15 EXAMPLE 6

Pickling and chromium tanning of sheepskin pelts

A solution of sodium formate (0.5%) and water (35%) was added to delimed pelts and the mixture drummed for 5 minutes. The phenol sulphonic acid mixture prepared in accordance with Example 1 or Example 2 (3.5% in water 10%) was added, and drumming was continued for a further 60 minutes, at which time pickling was close to equilibrium. Formic acid (0.4%) was added and drumming continued for another 30 to 60 minutes. Chromium powder (6% of 33% basic) was added, and full penetration was noted after 2 hours. The pH was raised to 3.5 to 4.2 over 3 hours by adding magnesium oxide, and the hides were drained and washed. Shrinkage temperature of the tanned material was $>100^{\circ}\text{C}$.

30 EXAMPLE 7

Low pH pickle of sheepskin pelts

Delimed pelts were drummed with water and sodium formate, then treated with phenol sulphonic acid solution as in Example 6. Drumming was continued for 2 hours and sulphuric acid (0.5%) was added. After further drumming

- 12 -

for 4 hours, antifungal agent was added, and the pelts were drummed for a further 1 hour. At a final pH of 1.2 no swelling was discernible.

EXAMPLE 8

5 Pickling of woolly sheepskins

As woolly sheepskins need a large float (i.e. a large amount of water) to prevent felting of the wool during processing, reagent concentration is very low and care needs to be taken when adding the phenol sulphonic acid in order to avoid swelling. This problem can be overcome as follows:

- 15 a) The woolly sheepskins were drummed in water (20 L per skin) containing sodium formate (2.5 g/L). After 1 hour, concentrated phenol sulphonic acid mixture (prepared as in Example 3) was added (15 ml/L), and the skins were drummed intermittently overnight. The final pH was 2.7, and no swelling was observed.
- 20 b) The woolly sheepskins were drummed for 15 minutes in water (20 L per skin) containing sodium formate (1.5 g/L) and sodium carbonate (2.5 g/L). Phenol sulphonic acid mixture (prepared as in Example 1 or 2) was then added (15 ml/L), and the skins drummed intermittently overnight. The
- 25 final pH was 3.1, and no swelling was observed.

While the present invention has largely been described with reference to chromium tanning, the invention can be expected to offer advantages when employed in association with other tanning regimes, such as other mineral tannages, vegetable tanning, aldehyde tanning, Syntans tannages, where pickling is required.

ADVANTAGES

- 13 -

The pickling process described herein produces a pickled stock of a quality virtually indistinguishable from that produced in the conventional salt/acid treatments; in addition to its effectiveness in suppressing swelling, it
5 offers the following advantages:

- It is salt free, and results in a significant reduction in the Total Dissolved Solids (TDS) in tannery effluent, thus making disposal of waste material more convenient.
- 10 - Using the method of the present invention, the addition of the pickling agent and the formation of the pickling agent is less hazardous and more convenient since only routine precautions need be taken. No specialised handling precautions or
15 specialised training and experience is required of operators.
- It does not require the handling of any solid material.
- The agent penetrates hides and skins as rapidly
20 as or more rapidly than the commercial salt alternatives referred to above.
- The agents can readily be used with the acids of the conventional salt/acid process.
- The agents are exhausted up to 70% or more.
- 25 - The pickled stock is compatible with conventional chromium or pickle recycling regimes, or tanning processes.
- The agents are inexpensive and easy to make.

- 14 -

5 - The final product obtained by the process of the present invention is just as good as the final product produced by conventional tanning since the quality of the leather produced by the method of the present invention is indistinguishable to that produced in conventional salt/acid tanning.

- The pickling formulation and pickling agent of the present invention are biodegradable.

- 15 -

CLAIMS

- 1) A method of treating a naturally derived product prior to performing a subsequent treatment wherein the naturally derived product is treated with a treatment agent to modify a property or characteristic of the naturally derived product, characterised in that the treatment by the treatment agent is effective at a final pH of or below 3.4 and in that the treatment agent comprises at least one or more of phenol mono-, di- or trisulphonic acid or derivatives thereof, either singly or in combination, including combination with other materials.
- 2) A method of preparing a treatment agent suitable for use in treating a naturally derived product to modify a property or characteristic of the naturally derived product, comprising contacting a phenol mono-, di- or trisulphonic acid or derivative thereof, either singly or in combination, including combination with other materials, with oleum or a sulphuric acid or an equivalent material, characterised in that the treatment agent is effective in modifying the property or characteristic of the naturally derived product at a final pH of about 3.4 or less.
- 3) A method according to any preceding claim, characterised in that the naturally derived product is a hide or skin suitable for use in producing leather or a leather product.
- 4) A method according to any preceding claim, characterised in that the treatment agent for use with the hide or skin is a pickling or acidifying agent.
- 5) A method according to any preceding claim, characterised in that the subsequent treatment is a tanning treatment, preferably a chromium tanning treatment.

- 16 -

- 6) A method according to any preceding claim,
characterised in that the treatment agent is a pickling
agent which comprises substantially pure phenol mono-, di-
or trisulphonic acids or mixtures thereof or derivatives
5 thereof.
- 7) A method according to any preceding claim,
characterised in that the other material is an acidic
material, preferably a sulphuric acid or oleum or
derivative thereof.
- 10 8) A method according to any preceding claim,
characterised in that the treatment agent comprises up to
and no more than about 1 g of sulphuric acid, oleum or
equivalent thereof per 1 g of the phenol sulphonic acid or
mixture thereof.
- 15 9) A method according to any preceding claim,
characterised in that the treatment agent comprises less
than about 0.6 g of sulphuric acid, oleum or equivalent
thereof per 1 g of the phenol sulphonic acid or mixture
thereof.
- 20 10) A method according to any preceding claim,
characterised in that the treatment agent comprises less
than about 0.4 g of sulphuric acid, oleum or equivalent
thereof per 1 g of the phenol sulphonic acid or mixture
thereof.
- 25 11) A method according to any preceding claim,
characterised in that the derivative of the phenol
sulphonic acid is any salt or partial salt or compound of
the phenol sulphonic acid or compounds having functional
groups equivalent to the phenol sulphonic acids including
30 compounds having a benzene ring substituted with a
sulphonic acid, carboxylate, ester, alkyl, hydroxyl or
thiol group.

- 17 -

- 12) A method according to any preceding claim, characterised in that the treatment agent comprises a mixture of phenol monosulphonic acid and phenol disulphonic acid, optionally together with phenol trisulphonic acid.
- 5 13) A method according to any preceding claim, characterised in that the amount of phenol disulphonic acid or phenol trisulphonic acid in the treatment agent is maximised in order to facilitate reduction in the amount of swelling of the hide or skins being treated.
- 10 14) A method according to any preceding claim, characterised in that the ratio of phenol monosulphonic acid to disulphonic acid is from about 100:1 to 1:100, preferably about 50:1 to 1:50, and more preferably is about 1:1 by weight.
- 15 15) A method according to any preceding claim, characterised in that the treatment agent is produced at a temperature from 0°C to 200°C, preferably in the range 80°C to 140°C.
- 20 16) A method according to any preceding claim, characterised in that the naturally occurring product is a hide or skin such as an ovine, porcine, bovine, caprine or similar hide or skin.
- 25 17) A method according to any preceding claim, characterised in that it is used in conjunction with or in combination with other tanning processes.
- 18) A method according to any preceding claim, characterised in that a treatment agent of from 1% to 10% by weight in water is used, based on the weight of the hide or skin being treated.
- 30 19) A method according to any preceding claim,

- 18 -

characterised in that the duration of the treatment of the skin or hide with the pickling solution is up to about 48 hours, preferably up to about 24 hours.

20) A naturally derived product treated by the method
5 of any preceding claim.

21) A pickling solution prepared by the method of any preceding claim.

22) A method substantially as hereinbefore described with reference to any one of the foregoing examples.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 95/00566

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C14C 1/04, 1/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : C14C 1/00, 1/04, 1/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU,A,32070/93 (CIBA-GEIGY) 29 July 1993 Examples	1-22
X	DE,A,1222618 (BADISCHE ANILIN - & SODA - FABRIK AKTIENGESELLSCHAFT) 11 August 1966 Whole document	1-22
A	AU,A,80829/75 (DIAMOND SHAMROCK CORPORATION) 11 November 1976 Whole document	1-22



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
16 November 1995

Date of mailing of the international search report
21 NOVEMBER 1995 (21.11.95)

Name and mailing address of the ISA/AU
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA Facsimile No.: (06) 285 3929

Authorized officer

GAYE HOROBIN
Telephone No.: (06) 283 2069

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 95/00566

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU,A,16688/88 (HOECHST A.G.) 1 December 1988 Whole document	1-22
A	US,A,1794920 (POSPIECH) 3 March 1931 Whole document	1-22

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 95/00566

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	1794920						
AU	80829/75	BR	7502725	FR	2270325	JP	50148502
DE	1222618						
AU	32070/93	BR	9300294	EP	554216	JP	5247498
		US	5360453	ZA	9300579		
AU	16688/88	BR	8802565	DE	3717829	EP	293705
		JP	63309600	NZ	224788	US	4935031
							END OF ANNEX

THIS PAGE BLANK (USPTO)